Pollutant Formation in the Pyrolysis and Combustion of Materials Combining Biomass and E-waste

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ABSTRACT

Combustion and pyrolysis runs at 850 ºC were carried out in a laboratory scale horizontal reactor with different materials combining biomass and waste electrical and electronic equipment (WEEE). Analyses are presented of the carbon oxides, light hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), polychlorinated benzenes (ClBzs), polychlorinated phenols (ClPhs), polybrominated phenols (BrPhs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). Results showed that gas emissions were mainly composed of CO and CO_2; the high level of CO found in the pyrolytic runs was easily transformed into CO_2 by reaction with oxygen. The total amount of light hydrocarbons emitted was somewhat higher in the samples containing WEEE, methane being the most abundant light hydrocarbon in all the runs. However, the presence of WEEE reduced the emission of PAHs which clearly decreased with the increase of the oxygen. The total amount of BrPhs increased in the decomposition of the samples containing WEEE, reaching its maximum in pyrolysis runs. Emission of PCDD/Fs was enhanced in pyrolytic conditions and they were easily destroyed in the presence of oxygen.

Keywords: WEEE, biomass, PAHs, Dioxins, Pyrolysis, Combustion.

1. Introduction

There is a worldwide soaring demand and sale of new electrical and electronic equipment, due to rapid economic growth and urbanization. As a result, the quantity of waste electrical and electronic equipment (WEEE) is ever-increasing, representing more than 5% of municipal solid wastes (MSW) (Nathanson, 2015). In 2014, according to United Nations University report (Baldé et al., 2015), 41.8 million tonnes of WEEE were produced worldwide. WEEE is composed of numerous materials, from recyclable raw materials such as plastics and metals (Cu, Al, Fe, Sn, Co, In, Sb and precious metals like Ag, Au, Pd and Pt) and hazardous products such as heavy metals (Cd, Hg, Pb and Ni) and halogenated (mainly brominated) flame retardants (Buekens and Yang, 2014). Consequently, WEEE represents a hazard to human life and the environment if not properly treated.

Electric wires (EWs) and printed circuit boards (PCBs) are some of the most complex constituents of WEEE, because they are composed of a great variety of organic materials and metals. This waste can be separated into metallic fraction (MF) and non-metallic fraction (NMF). The MF represents around 50% of the weight content of EWs, mainly constituted by Cu (Conesa et al., 2013), and 30% of the weight content of PCBs, consisting of Cu, Sn, Pb, Fe, Ni and noble metals (Goosey and Kellner, 2003). The rest is NMF that is made up of plastic materials, brominated flame retardants (BFRs) and other additives (Guo et al., 2009).

In the past, NMFs were treated by incineration (Kim et al., 2015) or were accumulated in landfills (Ning et al., 2017). However, incineration is considered to be significant source of emission of PCDD/Fs (Zhou et al., 2015) while landfilling can lead to contaminating the soil and groundwater by the leachate, which contains brominated toxic compounds as well as heavy metals (Akcil et al., 2015; Hadi et al., 2015) and by evaporation of hazardous substances (Guo et al., 2012).

Today, NMFs are much more valuable because they are suitable for recycling as well as for material or energy recovery. NMFs recycling techniques can be generally classified into physical or chemical recycling techniques (Guo et al., 2009). On the one hand, main applications of the physical recycling techniques of these fractions are as follow: filler for thermosetting resin matrix composites, reinforcing filler for thermoplastic resin matrix composites, raw material for concrete and modifier for viscoelastic materials. On the other hand, chemical recycling techniques, which include pyrolysis, gasification, supercritical fluids depolymerization and hydrogenolytic degradation, are used to convert the NMFs into chemical feedstocks and fuels. Despite the fact that recycling technologies are increasingly used in industrialized countries, most NMFs are still being accumulated in landfills or are being incinerated, because the uses of recycled NMFs are unprofitable (Duan et al., 2016).

Furthermore, in developing countries, many people tend to burn MSW together with wood, paper and cardboard waste in their household (Maasikmets et al., 2016). Households probably carry out this practice either to reduce fuel costs or to avoid disposal fees (Watson, 2012). However, waste burning in domestic conditions is a significant source of air pollutants. Incomplete combustion often occurs during domestic heating, where in the presence of chlorine, organic material causes the formation of chlorinated organic by-products, such as ClBzs or PCDD/Fs (Hedman et al., 2006).

Regarding environmental impacts, numerous studies examine pollution associated with metal-free WEEE combustion and/or pyrolysis (Aracil et al., 2005; Barontini and Cozzani, 2006; Barontini et al., 2005; Conesa et al., 2013; Duan et al., 2011; Ortuño et al., 2014a; Quan et al., 2012). However, no study has investigated pollutant emissions resulting from thermal degradation of materials combining biomass and metal-free WEEE. Only a few authors have analyzed pollutants emitted during thermal decomposition of materials combining biomass and other kinds of MSW. Maasikmets et al. (2016) studied pollutant emissions from the residential combustion of wood with MSW and obtained high emissions of PCDD/Fs and hexachlorobenzenes (HCBs). Edo et al. (2016) evaluated the emissions of PCDD/Fs from the torrefaction of waste wood with MSW and wood pellets with MSW. Lundin et al. (2013) examined the reduction of persistent organic pollutants (POPs) emissions during combustion of biomass with waste products from the pulp and paper industry.

In line with this research, the aim of this work is to study the thermal decomposition of two materials combining biomass (wood) and two different metal-free WEEE samples (EWs and PCBs) to determine pollutant emission under different operating conditions in a laboratory scale reactor. Previous modelling attempts have suggested that the use of these materials may reduce combustion efficiency and lead to an increase in toxic air pollutants (Conesa and Soler, 2016).

2. Materials and methods

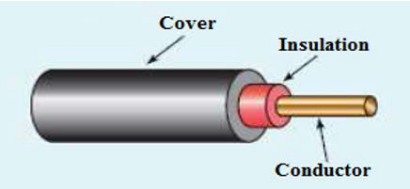
2.1. Biomass: crushed wood pellets (CWP)

Energías Renovables Tarazona S.A. (Spain) supplied the wood pellets which were crushed to fine dust using a vibratory disc mill RETSCH RS200, forming what will be called crushed wood pellets (CWP). Characterization of this CWP and a complete thermogravimetric study about its thermal decomposition under inert and oxidative atmospheres has been published previously (Conesa and Soler, 2016). The results of the elemental analysis are 51.56 wt.% C, 6.53 wt.% H and 40.79 wt.% O. The ash content was 1.13 wt.%.

2.2. Electric wires (EWs)

The EWs used in the present study are fire-resistant halogen-free wires. They were supplied by General Cable, Co (Spain). Figure 1 shows the scheme of the electrical wire, the composition of

the material used and the weight percentage of each part. As shown in Figure 1, the cover material is a mixture of polyethylene, a thermoplastic elastomer, and aluminum trihydroxide (PE-TPE-ATH) and the insulation material is a silicone rubber. Elemental analysis and some other details about the halogen-free wire can be found in a previous study (Conesa et al., 2013).



PART	HALOGEN FREE WIRE wt.%
Cover	Thermoplastic polyolefin (PE-TPE-ATH), 36%
Insulation	Silicone rubber, 20%
Conductor	Copper, 44%

Figure 1. Scheme of the electrical wire, its composition and weight percentage of each part.

In this study, only the NMF was used, which was manually separated from the MF and was shredded to a particle size smaller than 1 mm using a cutting mill RETSCH SM200.

2.3. Waste printed circuit boards (WCBs)

The WCBs employed were metal-free FR-4 circuit boards, supplied by Circuitos Impresos S.A (Spain). The FR-4 circuit boards were made of woven fiberglass cloth base epoxy resin flame retardant. These FR-4 circuit boards use tetrabromobisphenol A (TBBPA) as BFR (Soler et al., 2017).

The WCBs were manually cut into 2 cm x 2 cm using pliers and were crushed to fine dust using the vibratory disc mill RETSCH RS200. Elemental analysis, ash content and the concentration of bromine and chorine of this material can be found in a previous study (Soler et al., 2017).

2.4. Biomass and WEEE mixtures

For the decomposition runs, three different samples were tested. One sample of CWP was used as reference to compare the emissions, one sample combined CWP with EWs and another sample combined CWP with WCBs in a proportion of 20 % of waste (CWP+20% EWs and CWP+20% WCBs). The mixtures were ground again in a cryogenic ball mill (RETSCH CryoMill) to guarantee the homogeneity of the samples. A thermogravimetric study analogous to that of the CWP samples was carried out with these mixtures (Conesa and Soler, 2016).

2.5. Experimental system

Combustion and pyrolysis runs were carried out in a moving tubular reactor, which consisted in a quartz tube (10 mm internal diameter) where the material was introduced in three quartz boats (70 mm long each) along the tube. This experimental system has been described in detail previously (Conesa et al., 2013).

Once the process programmed temperature was reached (850 ºC in all runs), the boats were introduced in the horizontal furnace at constant speed using a horizontal actuator. Synthetic air (combustion runs) or nitrogen (pyrolysis runs) were introduced in parallel to the sample, with a constant flow of 500 mL min^{-1} (measured at 1 atm and 20 ºC). The sample mass in each run was

between 1.00 and 1.50 g. Before the decomposition runs, a control run containing no sample was carried out using the same experimental conditions (blank).

In the present study, the effect of the presence of oxygen in pollutant formation was examined by varying the oxygen ratio (λ). This ratio is defined as the fraction between the actual and the stoichiometric air flow rate necessary for a complete combustion (Conesa et al., 2009; 2011). In this way, the oxygen ratio is $\lambda=0$ for pyrolysis processes, and $\lambda=1$ for complete combustion processes where the oxygen present is the stoichiometric; $\lambda>1$ indicates processes with an excess of oxygen. In the present study, the oxygen ratio was modified by changing the input speed of the boats: values of $\lambda=0$ (pyrolysis), $\lambda=0.17$, $\lambda=0.50$ and $\lambda=0.70$ were considered.

Reproducibility of these types of experiments was addressed in our laboratory. A previous study (Garrido et al., 2016) confirmed good reproducibility for all compounds analyzed in emissions from combustion and pyrolysis runs of wastes using a similar laboratory scale horizontal reactor. Obtained standard deviations were small in comparison with the average values; standard deviations were somewhat greater only for some small average values, but with relative standard deviations around 5%.

The outlet gas stream of each run was sampled to analyze the following pollutants:

- Gases and volatile compounds were collected using Tedlar® bags (Restek, USA). CO_2 and CO were analyzed by gas chromatography with a thermal conductivity detector (GC-TCD) (Agilent 7820A GC) using two packed columns (Haye Sep Q 80/100 and Molecular Sieve 5A 80/100, both from Teknokroma, Spain) coupled with a pneumatic valve. Light hydrocarbons were analyzed by gas chromatography with flame ionization detector (GC-FID) (Shimadzu GC-17A) using an Alumina KCl Plot capillary column (Sigma-Aldrich, USA).

- PAHs, ClPhs, ClBzs, BrPhs and PCDD/Fs were collected in a polyaromatic Amberlite® XAD-2 resin (Supelco, Bellefonte, USA) placed at the exit of the furnace during the whole experiment. The Tedlar® bag was located after the resin.

Internal standards were employed to calculate the concentration of PAHs, ClPhs, ClBzs, BrPhs and PCDD/Fs in the samples. Dr. Ehrenstorfer-Schäfers (Augsburg, Germany) supplied the deuterated standards used for the analysis of the PAHs and Wellington Laboratories (Ontario, Canada) supplied the ^{13}C-labeled standards for ClPhs, ClBzs, BrPhs and PCDD/Fs. All the internal standards were added to the resin before the extraction.

The resin was then successively extracted with a mixture of dichloromethane/acetone (1:1 vol) and toluene by Accelerated Solvent Extraction (ASE-100 Dionex-Thermo Fisher Scientific, California, USA) following the US EPA method 3545A (US EPA, 2000). The extract was divided into two fractions: approximately 30 wt.% was used for the analysis of PAHs, ClPhs, ClBzs and BrPhs and the remaining 70 wt.% was employed for the analysis of PCDD/Fs.

PAHs, ClPhs, ClBzs and BrPhs were analyzed by GC-MS (Agilent GC 6890N/Agilent MS 5976N, Agilent Technologies, USA) following the U.S. EPA method 8270D (US EPA, 2007) as reference. A capillary column HP-5 MS (30 m × 0.25 mm × 0.25 μm, Agilent, USA) was employed for the analysis of PAHs and ClBzs, whereas a ZB-5MSi (30 m × 0.25 mm × 0.25 μm, Phenomenex, USA) was used for the analysis of ClPhs and BrPhs. The injection volume was 1 μL in split 1:25 for the analysis of PAHs and in splitless mode for ClBzs, ClPhs and BrPhs. The oven temperature program for the analysis of PAHs, ClBzs and ClPhs consisted of a first isothermal step at 40 ºC (5 min hold) then heating up to 290 ºC at 12 ºC/min (6 min hold) and finally heating up to 320 ºC at 20 ºC/min (10 min hold). The oven temperature program for the analysis of BrPhs started at 60 ºC (10 min hold), then 15 °C/min to 220 °C and finally 25 °C/min to 320 °C (15 min hold). The detection and quantification of the 16 priority PAHs (US EPA, 1998) from the analysis in SCAN mode, were performed with a standard of each compound by calibration comparing the spectra and the retention time of the primary ion. ClBzs, ClPhs and BrPhs were analyzed in the SIR mode and the identification of each isomer was performed comparing the retention times and the primary/secondary ion area ratio with that obtained in the calibration with the labelled compounds.

For the analysis of PCDD/Fs, a cleanup step was performed using the Power Prep automated system (FMS, Inc., Boston, MA) with three different columns: multilayer silica, basic alumina and activated carbon. The purified extract was analyzed by HRGC-HRMS using an Agilent HP5890 gas chromatograph equipped with programmable temperature vaporization (PTV) inlet, coupled to a Micromass Autospec Ultima-NT mass spectrometer. A DB-5MS chromatographic column (60 m x 0.25 mm x 0.25 μm, Agilent, USA) was used for this analysis, using a 5 μL injection volume. The oven temperature program for the analysis of PCDD/Fs consisted of a first heating up to 200 ºC at 40 ºC/min, then heating up to 235 ºC at 3 ºC/min and finally heating up to 300 ºC at 5 ºC/min (27 min hold). The recoveries obtained for the labelled standards were within the ranges established by the reference U.S. EPA method 1613 (US EPA, 1994).

3. Results and discussion

3.1. Gases and volatile compounds

Results for carbon oxides and light hydrocarbons analyzed by GC-TCD and GC-FID for combustion and pyrolysis runs at 850 ºC are shown in Table 1. CO and CO_2 were the main gaseous compounds to be emitted. The CO and CO_2 yields obtained in the combustion runs were much higher than those detected in pyrolysis at 850 ºC due to the fact that the increase of oxygen content in the atmosphere intensified the fuel combustion. The evolution of carbon oxides can also be analyzed with the oxygen ratio (λ). It was expected that the more oxygen content there was in the atmosphere, the more CO_2 and the less CO would be present in the gas.

This trend occurred in all runs at 850 ºC, regardless of the sample (CWP, CWP+20% EWs and CWP+20% WCBs).

The carbon oxides detected in the emissions from the three pyrolysis runs are due to the content of oxygen from the polymeric compounds of the samples. In a similar way, de Marco et al. (2008) found notable amounts of CO and CO_2 emitted from pyrolysis at 500 ºC of a sample obtained from a WEEE recycling plant.

Table 1 also presents the values of the mass ratio (R_{CO}) between CO and ($CO+CO_2$), as an indication of the quality of the combustion. As shown, at λ=0.7 the amount of CO produced is null, indicating that there was much oxygen in the run as required. Other materials (Rey et al., 2016) need a much higher value of λ to produce a low amount of CO.

207 **Table 1.** Yields of gases and volatile compounds during the thermal decomposition experiments at 850ºC.

EXPERIMENT	**Pyrolysis (λ=0)**			**Combustion (λ=0.17)**			**Combustion (λ=0.50)**			**Combustion (λ=0.70)**		
SAMPLE	**CWP**	**CWP + 20 % WCBs**	**CWP + 20 % EWs**	**CWP**	**CWP + 20 % WCBs**	**CWP + 20 % EWs**	**CWP**	**CWP + 20 % WCBs**	**CWP + 20 % EWs**	**CWP**	**CWP + 20 % WCBs**	**CWP + 20 % EWs**
COMPOUND	**mg / kg sample**											
Analysis by GC-TCD												
CO	199300	216000	227600	226200	302300	242500	176700	155200	177500	nd	nd	nd
CO_2	118600	85700	107700	287800	328800	304300	1339100	1294400	1592800	1560700	1323700	1381500
R_{CO}=CO/(CO+CO_2)	0.63	0.72	0.68	0.44	0.48	0.44	0.12	0.11	0.10	0	0	0
Analysis by GC-FID												
methane	49930	45670	47020	12130	10040	12830	1210	1330	1720	200	210	220
ethane	2940	2730	2530	350	630	480	30	110	50	20	30	nd
ethylene	40740	26510	27100	5740	11900	10440	1660	1260	2010	150	150	180
propane	170	110	20	nd	240	10	nd	nd	nd	nd	nd	nd
propylene	40	40	nd	nd	20	nd	nd	nd	nd	nd	nd	nd
isobutane	6660	6070	5840	nd	nd	nd	nd	nd	nd	nd	nd	nd
acetylene	640	640	580	600	670	510	480	550	480	160	210	320
isobutene	130	140	120	nd	nd	nd	nd	nd	nd	nd	nd	nd
cis-2-butene	190	40	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
propine	40	30	180	nd	310	220	30	nd	40	nd	nd	nd
1,3-butadiene	5110	4670	4610	nd	nd	nd	30	nd	50	nd	nd	nd
2-butine	1210	1190	870	nd	nd	nd	30	nd	60	nd	nd	nd
1-butine	40	20	nd	nd	20	70	nd	nd	nd	nd	nd	nd
n-hexane	3670	3340	3080	nd	nd	nd	20	nd	40	nd	nd	nd
n-heptane	170	nd	nd	nd	30	30	nd	nd	nd	nd	nd	nd
toluene	80	30	nd	40	90	50	170	100	280	20	410	730
TOTAL	**111760**	**91230**	**91950**	**18860**	**23950**	**24640**	**3660**	**3350**	**4730**	**550**	**1010**	**1450**

208 nd: not detected (<10 mg/kg sample)

The main light hydrocarbons were methane and ethylene for both pyrolysis and combustion runs. This result agrees with the findings of a study by Grieco and Baldi (2012) which reported that the most abundant light hydrocarbons were methane and ethylene for pyrolysis of polyethylene (PE) mixed with wood.

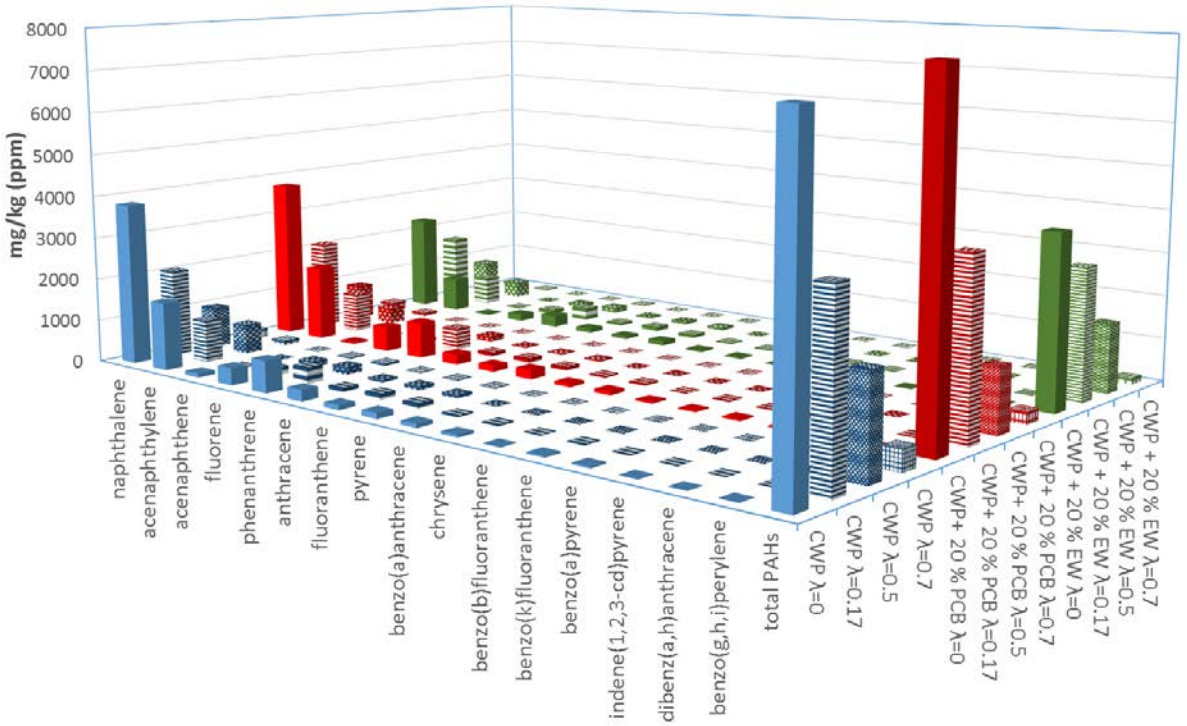
Under pyrolytic conditions light hydrocarbons showed higher yields, which indicates that these compounds react with oxygen in combustion runs (Conesa et al., 2009; 2000). These compounds are considered final products from cracking reactions occurring at high temperatures and show a maximum at 850 ºC, as also observed by Moltó et al. (2011; 2009).

With respect to the effect of the presence of oxygen at high temperature, light hydrocarbons yield decreased with the increase of λ (as shown in the last row in Table 1). In this way, emitted hydrocarbons in the CWP series, when comparing λ=0 with λ=0.7, are reduced by more than 99.5%. It is also important to note that emitted hydrocarbons are reduced with the presence of both EWs or WCBs in pyrolytic conditions, but the emission is somewhat higher in the combustion runs at a different λ. This would indicate (together with the values of the R_{CO} ratio) that combustion is slightly poorer in the presence of these wastes, although the emitted hydrocarbons are also easily reduced in the presence of oxygen.

3.2. PAHs, ClBzs, ClPhs and BrPhs

Figure 2 shows the results of the emissions of the 16 priority PAHs for all the runs. Data is also provided in Table SM1 of the Supplementary Material. The dominant PAH was naphthalene, followed by acenaphthylene, phenanthrene and fluorene. Naphthalene is clearly the most abundant product formed during thermal decomposition of different wastes at the same temperature (Conesa et al., 2009; Zhou et al., 2015). This occurred also in residential combustion of MSW and wood where 80% - 95% of total PAHs emissions were naphthalene, acenaphthylene, fluorene and phenanthrene (Maasikmets et al., 2016).

All the samples followed similar trends for each experimental condition, with a maximum formation of PAHs under pyrolysis as expected, since pyrolytic processes are known to be the primary source of PAH formation (Thomas and Wornat, 2008). With respect to the effect of the presence of oxygen, the PAH emissions clearly decreased with the increase of the oxygen content in the atmosphere for all the samples. These results agree with a previous study (Fullana et al., 2000) which reported that PAHs are pyrolytic products that are easily eliminated in oxygen rich environments at 850 ºC.



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241 **Figure 2.** Emissions of PAHs (mg/kg sample).

242 Comparing the results of the emissions of CWP and mixtures of CWP with EWs and WCBs, it
243 seems that the presence of EWs reduces the emissions of PAHs, whereas the presence of WCBs
244 does not have any effect on emissions. This should be related to the nature of the materials, but
245 also to the interaction between them. In this sense, a previous study (Conesa and Soler, 2016)
246 showed that the interaction between CWP and EWs is much stronger than the CWP-WCB
247 interaction, especially in the presence of oxygen.

248 Using the toxic equivalency factors published in literature (Nisbet and LaGoy, 1992), it is
249 possible to estimate a value of carcinogenic potential (KE) from the emission data of PAHs.
250 Values of KE for pyrolysis runs vary between 30 and 67 mg/kg, corresponding the lowest value
251 to the decomposition of CWP + 20% EWs. This shows that the incorporation of such wastes
252 into the fuel does not increase the toxicity of the emission of these pollutants. Previous studies
253 showed that the thermal decomposition of other biomass feedstock, such as coffee husk, could
254 produce even more toxic emissions, with a value of KE = 120 mg/kg reported at the same
255 decomposition temperature (Conesa et al., 2016).

256 A relatively low quantity of ClBzs was detected (Table SM2 in the Supplementary Material)
257 during thermal decomposition at 850 ºC. Total yields of ClBzs were almost negligible and
258 varied between the 0-0.41 mg/kg sample for the CWP, 0.18-4.91 mg/kg for CWP+20% WCBs,
259 and 0.11-6.63 mg/kg for CWP +20% EWs. The experiments with the highest total yields were
260 pyrolysis runs, obtaining the maximum total yield for the sample of CWP +20% EWs. No clear

trend was found in the ClBzs congener profiles, but mono-, di- and trichlorinated congeners were the main ClBzs to be emitted.

The yields of ClPhs were almost negligible in all the combustion runs. They are shown in Table SM3 (Supplementary Material). The highest yields of ClPhs were observed in pyrolytic conditions; in such a way that the yields decreased with the presence of oxygen, consistent with the profile of PAHs. This was also the tendency during the thermal decomposition of other wastes (Garrido et al., 2017; Rey et al., 2016). The maximum total yield of the 2.7 mg/kg sample was obtained for the sample of CWP.

Regarding specific congener profiles, monochlorinated phenols (3-+4-) were the most abundant products, in accordance with results obtained by Kaivosoja et al. (2012) in their study on pollutant emissions from residential wood combustion. The second most abundant one was 3,4,5-TriClPh, which agrees with the observed by Garrido et al. (2017) during pyrolysis of viscoelastic memory foam. ClPhs are considered to be the most direct precursors of the formation of PCDD/Fs (Ballschmiter et al., 1988; Sidhu et al., 1995) and these are among the most abundant aromatic compounds found in MSW incineration emissions (Tuppurainen et al., 2000).

Table 2 shows the results of the isomer specific analysis of BrPhs for all experiments. As in the case of ClPhs, total yields were nearly negligible, except for the sample of CWP+20% WCBs. Regardless of the sample, the formation of BrPhs was greater in pyrolytic conditions than in oxidative ones. The total BrPh yields decreased with the increase of the oxygen ratio, as observed for the rest of pollutants. The maximum total yield of 79.0 mg/kg was obtained when pyrolyzing the sample of CWP+20% WCBs. This result can be explained by the marked initial bromine content of this sample, as TBBPA is the flame retardant present in the used WCBs (Soler et al., 2017).

285 **Table 2.** Yields of brominated phenols (BrPhs) during the thermal decomposition experiments at 850 ºC.

EXPERIMENT	**Pyrolysis (λ=0)**			**Combustion (λ=0.17)**			**Combustion (λ=0.50)**			**Combustion (λ=0.70)**		
SAMPLE	**CWP**	**CWP + 20 % WCBs**	**CWP + 20 % EWs**	**CWP**	**CWP + 20 % WCBs**	**CWP + 20 % EWs**	**CWP**	**CWP + 20 % WCBs**	**CWP + 20 % EWs**	**CWP**	**CWP + 20 % WCBs**	**CWP + 20 % EWs**
COMPOUND	**mg / kg sample**											
2-	0.05	46.7	0.06	0.02	4.87	0.11	nd	0.04	nd	nd	0.04	nd
3-+4-	0.08	7.02	nd	0.01	2.47	0.06	nd	0.07	nd	nd	0.04	nd
2,4-	nd	4.40	0.12	nd	0.38	nd	nd	nd	nd	nd	nd	nd
2,3-+2,5-	nd	nd	0.06	nd	nd	nd	nd	nd	nd	nd	0.01	nd
2,6-	nd	20.5	0.14	nd	1.05	0.01	nd	nd	nd	nd	nd	nd
3,5-	nd	nd	nd	nd	0.15	0.06	nd	nd	nd	nd	nd	nd
3,4-	nd	0.08	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2,3,5-	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2,4,6-	nd	0.31	nd	nd	0.21	0.01	nd	nd	nd	nd	nd	nd
2,3,4-	nd	nd	nd	nd	nd	nd	nd	0.02	nd	nd	nd	nd
2,4,5-	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2,3,6-	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
3,4,5-	nd	nd	nd	0.03	nd	nd	nd	0.28	nd	nd	0.21	nd
2,3,5,6-	nd	nd	nd	0.01	nd	nd	nd	nd	nd	nd	nd	nd
2,3,4,5-+2,3,4,6-	nd	nd	nd	0.02	0.01	nd	nd	nd	nd	nd	nd	nd
penta-	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
TOTAL BrPhs	0.13	79.0	0.38	0.09	9.15	0.25	nd	0.41	nd	nd	0.30	nd

286 nd: not detected (<0.01 mg/kg sample)

With respect to congener distribution, as occurred in the case of ClPhs, monosubstituted congeners predominated, followed by dibrominated phenols. In particular, 2-BrPh was the most abundant compound, followed by 2,6- and 2,4-diBrPh; this concurs with the formation pattern observed for emission from thermal degradation of tetrabromobisphenol A (Ortuño et al., 2014b). Predominance of these congeners was also found in thermal decomposition of PCBs which contained TBBPA as BFR (Barontini and Cozzani, 2006; Barontini et al., 2005; Grause et al., 2008; Ortuño et al., 2014a).

Not many references were found in the literature to compare the results obtained for PAHs and no data were found about the formation of chlorobenzenes, chlorophenols and bromophenols in thermal decomposition of materials combining biomass and WEEE.

3.3. Dioxins and furans (PCDD/Fs)

Table SM4 (Supplementary Material) shows the amounts of the different PCDD/F congeners emitted in pg/g sample. All the samples presented undetectable amounts of most congeners of PCDD/Fs. Total PCDD/F emission, shown in Figure 3, was much higher in pyrolysis. The total amount was approximately 17.8 pg WHO-TEQ/g for the pyrolysis of CWP, 50.7 pg WHO-TEQ/g for CWP+20% WCBs and 56.1 pg WHO-TEQ/g for the CWP+20% EWs. These values were fairly lower than the emission measured in a similar experimental system for other materials, such as sewage sludges (630 pg WHO-TEQ/g), used oils (80 pg WHO-TEQ/g) or PVC (4500 pg WHO-TEQ/g) and similar to that presented by meal wastes (12 pg WHO-TEQ/g), cotton textiles (8 pg WHO-TEQ/g) and polyester textiles (16 pg WHO-TEQ/g) (Conesa et al., 2009). Furthermore, this emission was quickly destroyed in the presence of oxygen, with PCDD/F emission lower than 12 pg WHO-TEQ/g, in all cases for λ>0.1.

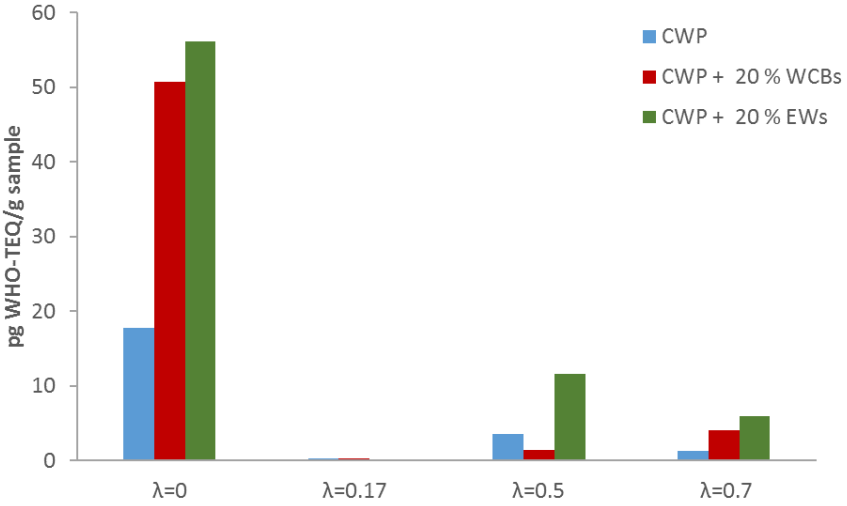

Figure 3. Total emission of PCDD/Fs obtained in pyrolysis and combustion runs at 850 ºC.

311 The values from the combustion runs were much lower than the emission in the torrefaction of
312 waste wood with MSW (246 pg/g fuel) (Edo et al., 2017). In pyrolysis, the most abundant
313 congeners in all samples were 12378-PeCDD and 23478-PeCDF, which were also detected in
314 the combustion runs. Maasikmets et al. (2016) observed that levels of PCDD/Fs were higher
315 than the legal limit for combustion in MSW incineration plants (European Commission, 2010),
316 being 23478-PeCDF and 2,3,7,8-TCDF the ones with the highest values.

317 # 4. Conclusions

318 This study presented pollutant emissions from thermal decomposition of mixtures of biomass
319 (CWPs) and wastes (EWs and WCBs) under different conditions. Experiments were performed
320 under inert and oxidizing atmosphere at 850 ºC.

321 In addition to CO and CO_2, methane and ethylene were the main compounds emitted during the
322 decomposition of the samples, their yields decreasing with the increase of oxygen content in the
323 atmosphere.

324 For all the samples, the most abundant PAH was naphthalene, with higher total yields in
325 pyrolytic conditions. However, global toxicity of the emissions for all runs, measured using the
326 KE index, was relatively low compared to other materials.

327 ClBzs, ClPhs and BrPhs yields were almost negligible. Maximum BrPhs emission was obtained
328 when pyrolyzing the sample containing CWP and WCBs, due to the high bromine content in
329 WCBs because of the presence of TBBPA.

330 PCDD/F emission was destroyed in the presence of oxygen. The highest total emission was
331 found in pyrolysis for all the samples, as occurred in the case of the rest of pollutants studied,
332 12378-PeCDD and 23478-PeCDF being the most abundant PCDD/F congeners.

333 Results obtained indicate that the tendency to emit pollutant depended mainly on the
334 combustion conditions, i.e. the oxygen ratio. In addition, these results show that the
335 incorporation of this kind of WEEE, in the 20 wt.% studied, would not appreciably affect the
336 emitted pollutants during thermal decomposition.

337 # 5. Acknowledgments

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